Quantitative determination of molecular adsorption structures: STM and DFT are not enough

D. P. Woodruff

Physics Department, University of Warwick, Coventry CV4 7AL, UK

E-mail D.P.Woodruff@warwick.ac.uk

Abstract

There is now a range of well-established experimental methods for quantitative determination of the structure of crystalline surfaces with sub-ångström precision, but increasingly in recent years structure 'determinations' are being based *only* on a combination of scanning tunnelling microscopy (STM) images and density functional theory (DFT) calculations. The dangers and limitations of this approach are described using a few specific examples that illustrate the complementarity, rather than competitive use, of these two different approaches.

1. Introduction

It is axiomatic in understanding materials (both physical and biological) that *structure determines function,* so knowledge of the structure is the starting point for understanding functional properties. In the case of solid surfaces key functional properties are the chemical reactivity and the electronic properties. Heterogeneous catalysis relies on the fact that, on a surface, there are reaction routes available when one or more of the reactants is adsorbed that can circumvent the high energy barriers that prevent certain reactions occurring in the gas phase. Moreover, the electronic properties of conductor-semiconductor interfaces determine energy level alignment and electron transfer, defining the functionality of electronic devices. Despite this clear need for quantitative surface structure determinations, experiments to undertake these represent only a very small fraction of current surface studies. Well-established experimental structural methods are available (e.g. [1]), but they do require care and often time-consuming modelling calculations to interpret the data. Far more fashionable are qualitative surface studies based particularly on scanning tunnelling microscopy (STM). A second substantial change influencing modern surface science studies has been the major advances in the theoretical modelling of both structural and electronic properties of surfaces using density functional theory (DFT). In view of the success of these two techniques, it is not unreasonable that an increasing trend in investigations of surface structure is to combine STM and DFT, but it is less reasonable to use *only* these two techniques for structure 'determination'. In such studies it is *only* the DFT results that provide quantitative structural parameter values, so the resulting structure 'determination' ultimately relies entirely on the theoretical calculations. The objective of this short perspective review is to illustrate and evaluate the limitations of this approach.

2. STM and DFT- advantages and limitations

There is no doubt that the technique of STM has played a huge positive role in advancing our understanding of surfaces, and particularly the heterogeneity of surfaces in many

situations in which, for want of contrary information, a surface was often assumed to be perfectly homogeneous. STM provides real-space images of a surface with atomic resolution, although these images are of lateral variations in the electronic structure just outside the surface. These variations are related to atomic positions, but not in a trivial way. However, the seductive apparent simplicity of such images can easily lead a researcher to accept that 'seeing is believing', and assume that, in the most commonly used mode of operation at constant tunnelling current, all atomic-scale protrusions correspond to the positions of surface atoms. In fact there are ample examples of situations in which this is not true (e.g. [2]). For example, it has long been known that atomic oxygen or C adsorbed on metal surfaces leads to dips in the image, rather than protrusions, above these adsorbed atoms [3, 4], an effect that is due to the electronic character of the tunnelling probe and is generally well-understood theoretically [5]. The elegant simplicity of obtaining visually attractive data from a well-functioning scanning tunnelling microscope has unfortunately led to many publications that fail to follow the long-established rule of surface science that multiple complementary methods must be used to understand a system. For example, many such experiments fail to include any determination of the surface composition which can be easily obtained using X-ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES). Nevertheless, in studies of molecular adsorbates on single crystal surfaces of metal and other conductors, STM can certainly provide information on the lateral periodicity of ordered overlayers and can often provide strong indications of the molecular orientation through some sub-molecular resolution in the images. In experiments in which both the substrate atoms and the adsorbed molecules can be imaged simultaneously, it may also be possible to identify their lateral registry. Notice, though, that if both cannot be imaged simultaneously, it is difficult to distinguish with complete confidence between commensurate and incommensurate overlayer structures with large unit meshes. In this regard a standard diffraction technique such as low energy electron diffraction (LEED) (using only the observed diffraction pattern) can prove to be invaluable. LEED does show simultaneously diffracted beams associated with the substrate periodicity and the overlayer periodicity, and it is generally easy to establish if there is an exact integral relationship between the two. In the case of overlayers with large unit meshes that do not

share the point group symmetry of the substrate, LEED patterns, averaged over multiple symmetrically-equivalent domain orientations, can be rather difficult to interpret in isolation, but combined with approximate measurements of the unit mesh size in individual domains with STM, an accurate assignment of the surface mesh can be made rather readily. The combination of STM and LEED is ideal for this purpose.

Measurements of distances between molecules and atoms in identical local sites using an STM based on well-calibrated piezoelectric positioners do correspond to true intermolecular and interatomic distances parallel to the surface, because the electronic environments probed by the tip at these different locations are identical. Indeed, this is also true for measured distances perpendicular to the surface measured from equivalently located molecules on different atomic surface terraces. This is not true, however, for measurements between inequivalent positions in an image, due to the intrinsic electronic effects of the technique. In the context of quantitative surface structure determination, therefore, the only quantitative information that STM can contribute is the surface periodicity. In addition, however, images can provide a basis for proposing detailed qualitative structural models, albeit with the caveats concerning the interpretation of these images in terms of (approximate) relative atomic positions.

The second technique that has brought new understanding to surface science in the last one or two decades is density functional theory. Advances in the methodology and in the availability of high-speed computing facilities means that DFT can be applied rather reliably to metal surfaces (including those of high atomic number) and their interaction with adsorbed and interacting molecules. A typical DFT study of a surface structure effectively involves a search, for one or more structural models, of the set of structural parameter values that leads to the lowest total energy. The result provides optimised atomic coordinates and the electronic structure. .

There is no doubt that very many DFT studies have yielded structural and electronic properties of surface phases that have proved to be fully consistent with experimental evidence. There are also a few examples where this is not true. A particularly well-known

example is the case of CO adsorption on Pt(111); many calculations from the most respected groups found the energetically favoured adsorption site to be a local 3-fold coordinated hollow, whereas a similarly high quality set of experimental measurements found the true adsorption site to be atop a surface Pt atom [6]. While a number of subsequent studies found alternative DFT functionals able to achieve the correct result, this issue continues to be debated (e.g. [7]). In a number of other systems, different choices of DFT functional influence the preferred structure, the choice that best agrees with experiment not always being the functional generally regarded as superior (e.g. in a study of the orientation on CN adsorbed on Cu(111) and Ni(111) [8]). While such problems may be rare, it is only with the availability of experimental structural data that they can be recognised. The general precept that theory needs experiment to 'keep it honest' is as true in structural studies as it is in investigations of other properties.

A more general limitation of structure ‘determination’ by DFT calculations is that this method suffers from the same problem that underpins most experimental structure determinations. Specifically, essentially all of these experimental methods involve, at some stage in the process, a trial-and-error search of alternative structural models, comparing the experimental results with those of simulations based on a small number of structural models, and varying the structural parameter values in each model, until the best agreement with the experimental result is found. An underlying weakness of all of these experimental techniques, but also of DFT calculations, is that if the correct structural model is not tested, it cannot be found. The search algorithms built into modern DFT codes are efficient at finding the best set of structural parameter values for a given structural model, but cannot find a better model if it is not tested. While this is also true for experimental structural methods, if a best-fit structural model still gives poor agreement with experiment, this is a clear indication that the correct structural model has not been tested. There is no such warning signal in a similar DFT search

4. Case studies

A few case studies serve to illustrate some of the issues concerning the role of STM in solving surface structures in a fully quantitative fashion. Unfortunately, there are rather few examples of molecular adsorption systems for which sufficient complementary methods have been applied to be able to regard them as comprehensively solved with the highest degree of certainty. Nevertheless, two specific systems, together with less complete investigations of related systems, serve to illustrate the issues.

4.1 Thiol self-assembled monolayers on Au(111)

A particular example of the problem of failing to test the 'correct' structural model has frequently arisen from systems in which adsorption has eventually been found to change the atomic density of the outermost layer(s) of the underlying substrate. Substrate reconstruction models are obviously quite different from models based on adsorption alone (possibly with some relaxation of the underlying surface layer), and must be tested separately in applications of quantitative experimental structural studies. This is also true for structural searches with DFT; search algorithms do not consider the possibility of changing the number of atoms in the near-surface unit cell. Early manifestations of this effect were the so-called missing row structures formed on some surfaces by adsorbates. The best-known example of this is probably the Cu(110)(2x1)-O surface, on which the Cu atomic density of the outermost layer is reduced by 50% relative to an ideal bulk termination, due to the adsorption of atomic oxygen. In fact, after the basic structural model was established by several different experimental techniques, dynamic STM studies during oxygen dosing were finally understood [9, 10, 11] to show that this reconstruction occurs by the addition, rather than removal, of alternate <100> Cu surface rows of atoms (although the first such STM study [12] actually concluded the surface density was unchanged, highlighting the ambiguity of interpretation of pure STM studies). Of course, the ultimate equilibrium structure does not distinguish between added

rows and missing rows. They are equivalent. These early studies predated the use of DFT to investigate such structures.

Subsequently, the idea that atomic and molecular adsorbates on metals could induce reconstruction of the outermost atomic layer, in some cases with changes in the atomic density, became more widely recognised. One particularly extensively studied system for which this proved to be true is that comprising the archetypal 'self-assembled monolayers' (SAMs) formed by deprotonated alkane thiols, $CH_3(CH_2)_nS$- on Au(111). There is quite a range of different overlayer ordered structures formed depending on coverage and alkane chain length (the value of *n*), with the molecules apparently lying down at low coverage but standing up (albeit tilted) at higher coverages. However, a common feature of most of these standing-up phases is a periodicity relative to the substrate of (√3x√3)R30°, or a c(4x2) superstructure of this basic periodicity (more properly described as (2√3x√3)rect.). This information on the surface periodicity was established both by STM studies and by some X-ray and He atom diffraction studies. However, none of these experiments addressed a key question: what is the local adsorption site of the S head-group relative to Au(111) substrate? In the absence of any experimental information it was widely assumed that three-fold coordinated hollow sites were occupied, but as theoretical methods developed there was a flurry of DFT calculations undertaken from about 2000 onwards. Several of these favoured the previously expected hollow site (e.g. [13]), although others favoured two-fold coordinated bridge sites or a site intermediate between these two (references to many of these early studies may be found in a brief review in 2008 [14]). Notice that it was generally recognised that the complex 'herring-bone' reconstruction of the clean Au(111) surface is lifted by the adsorption, so it was assumed that adsorption was on an unreconstructed ideal bulk-terminated surface (111) surface. In fact two of these earlier DFT studies did find evidence of energetic preference for models with some Au surface vacancies, but still found that bridge or off-bridge sites occupation was favoured [15, 16]. However, shortly afterwards two independent experimental quantitative structural investigations of the local adsorption site, using different techniques (photoelectron

diffraction and normal incidence X-ray standing waves - NIXSW), provided clear evidence that the S headgroup atom actually occupies a site directly atop surface Au atoms [17, 18], and subsequently provided some less direct evidence that the outermost Au(111) surface may be reconstructed [19]. What is now the generally accepted model of the interface structure emerged from STM images at low thiol coverages (in which both the clean areas of the surface and the adsorbed molecules could be imaged with atomic resolution) combined with further DFT calculations. In this model Au adatoms bind to pairs of thiolate molecules to produce a local Au-adatom-dithiolate species on the surface [20]; the Au adatoms occupy bridging sites on the surface while the S headgroup atoms of the thiolates do, indeed, occupy near-atop sites (Fig. 1). Thus, while STM and DFT played a vital part in gaining this understanding of the structure of this surface, it was the need to revise the underlying structural model in the light of the results of experimental quantitative structural studies that fundamentally changed the previously accepted model of an unreconstructed surface with a completely different local bonding geometry (that was, itself, based on DFT calculations aided by STM observations of the surface periodicity).

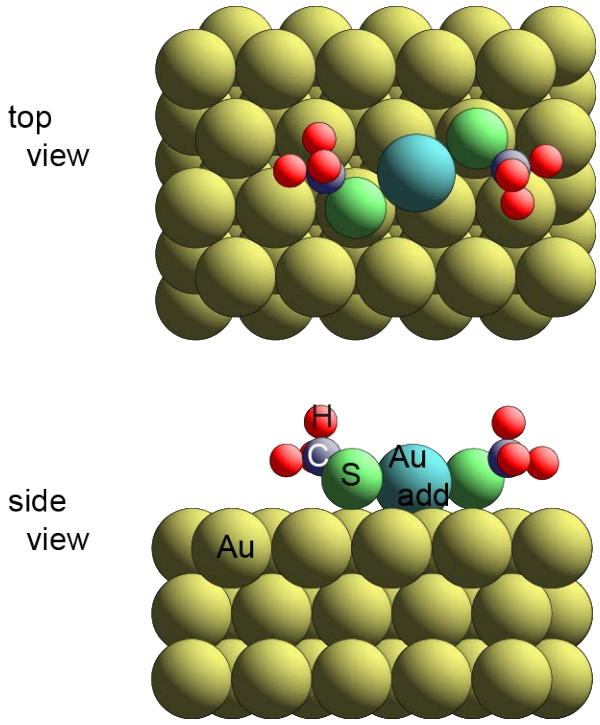

Fig. 1 Top and side views of a ball model of the local adsorption site of methylthiolate on Au(111) to create a dithiolate-adatom species. The Au adatom is shown in a different colour to those of the substrate for clarity.

4.2 Metal organic interface structures

A rather different type of molecular adsorption system that has attracted much attention in recent years has been of essentially planar molecules, of potential relevance to organic semiconductor devices, adsorbed on metal surfaces. The electronic structure at this type of metal-organic interface, and notably the energy alignment of the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) relative to the Fermi level of the metal, plays a crucial role in defining the functionality of any resulting device. This electronic structure can be strongly influenced by the geometrical structure of the interface, such as the molecule-substrate spacing and the role of any adsorbate-induced reconstruction. There are many published studies of such systems that rely entirely on the combination of STM and DFT with no experimental quantitative structural information. For these systems a matter of concern is not only the extent to which such studies have considered the full range of plausible structural models, including the influence of substrate reconstruction, but also the influence of different choices of DFT functional. In particular, the bonding of these molecules to the metal surface can be strongly influenced by van der Waals forces, which were not taken into account in the original formulation of density functional theory. In recent years there has been a lot of work undertaken to develop DFT functionals that address this problem, in part through semi-empirical methods but more recently by more consistent *ab initio* approaches (see, e.g. [21,22, 23]). The use of different functionals can lead to large variations (as much as ~ 1 Å) in the optimal height of the molecule above the surface, and this inevitably this leads to significant differences in the predicted electronic structure.

A recent example of a group of systems of this type, mainly studied recently only by STM and DFT, is provided by investigations of the molecule TCNQ (7,7,8,8-tetracyanoquinodimethane, see Fig. 2) adsorbed on coinage metal surfaces. TCNQ is a prototypical electron acceptor molecule able to form charge transfer salts with high electron conductivity that have been influential in the development of a range of electronic devices. The planar structure of TCNQ as a free molecule is very rigid, due to

the conjugated π-system that extends throughout the molecule. However, if one or more electrons are transferred to it, these become localised on the electron-withdrawing cyano groups and the central quinoid ring aromatises, disrupting the π-conjugation. The peripheral carbon atoms thus become sp^3 hybridised, rendering the molecule far more flexible. A number of DFT calculations for TCNQ (and F_4TCNQ) adsorbed on Cu, Ag and Au surfaces concluded that the molecule becomes strongly bent into an inverted bowl configuration, with the cyano N atoms bonding to the surface more than 1 Å below the quinoid ring.

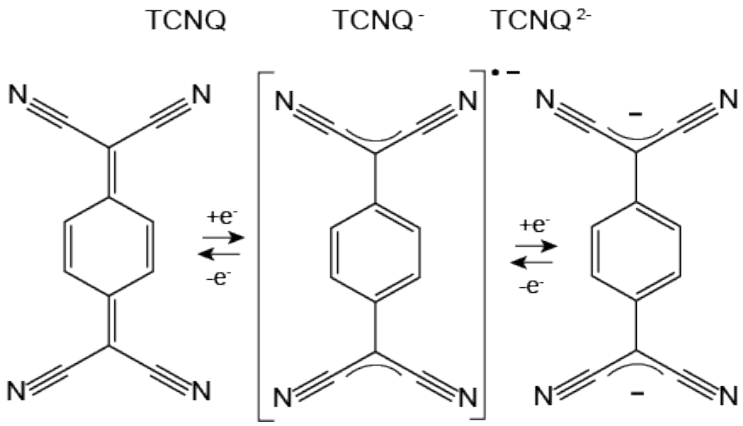

Fig.2. Bonding configurations of the TCNQ molecule in different charge states. In the neutral state the molecule has rigid π-conjugation. With added electrons the quinoid aromatises removing this rigidity.

However, a recent investigation of TCNQ adsorbed on Ag(111), that included the use of an experimental quantitative structural technique [24], shows that the true situation can be more complex than this. Specifically, a commensurate ordered $\begin{pmatrix} 2 & 5 \\ -8 & -2 \end{pmatrix}$ sub-monolayer phase, identified by STM and LEED, was investigated using NIXSW. A surprising result of these measurements was that the *average* heights of all of the constituent atoms in the adsorbed molecule were almost identical. The heights of the N atoms, the C atoms bonded only to N, and the C atoms between the CN and ring components differed by only 0.03±0.07 Å, although the C atoms bonded to H atoms were marginally (by 0.10±0.7 Å) higher. The implication that the adsorbed molecule remains planar is clearly not consistent with the expected strong bending in view of spectroscopic

evidence that there was significant electron transfer to the adsorbed TCNQ from the metal. However, a key additional piece of information provided by the NIXSW experiment was that the coherent fraction for the N atoms was very low (0.39). The coherent fraction in XSW studies is commonly regarded as an order parameter, but values less than ~0.7 are generally indicative of co-occupation of two or more different heights. Differences in heights of only two components can significantly lower this parameter; indeed, if two equally occupied heights differ by half the substrate layer spacing, the coherent fraction is zero, despite the system being perfectly ordered [25]. The fact that the coherent fraction for the N atoms was low led to a re-evaluation of the generally assumed structural model for TCNQ adsorption in which the substrate is unreconstructed. In particular, other structural models were investigated using DFT calculations to identify structures that not only correspond to the lowest total energy, but are also consistent with the experimental NIXSW structural data. This led to identification of a model containing Ag adatoms, which satisfied these conditions. Notice that the $\begin{pmatrix} 2 & 5 \\ -8 & -2 \end{pmatrix}$ phase contains three TCNQ molecules per unit mesh, so alternative adatom models could contain one, two or three Ag adatoms per unit mesh. The relatively small energy differences between these models led to the suggestion that in practice there may be a Boltzmann distribution of the different models, and the resulting mixed model gives good agreement with the experimental NIXSW parameters.

Fig. 3 shows side views of the local geometry of a single adsorbed TCNQ molecule resulting from three different DFT calculations. Specifically, results are shown for the lowest-energy reconstruction model, containing two Ag adatoms per unit mesh, and for the model with no Ag adatoms, in this case obtained from calculations with and without dispersion corrections to include the influence of van der Waals forces (labelled DFT-D and DFT, respectively). Notice that the calculated structures on the unreconstructed surface show the molecule to be significantly more strongly bent in the calculations that lack dispersion corrections than in calculations that include these corrections. The height of the bonding N atoms above the surface is almost the same (within 0.04 Å) in the two calculations, but the quinoid centre is 0.5 Å higher without the inclusion of the dispersion

correction. The important influence of the dispersion force corrections on the overall adsorption height for molecules of this type is well established, but the very significant influence on the shape of the molecule was not anticipated. Most of the earlier DFT calculations that helped to establish the conventional wisdom regarding the change in the molecule shape were based on calculations with no dispersion correction, a further indicator of the danger of relying only on these computed structures. Notice, too, that not all DFT-D functionals lead to the same adsorption height; the NIXSW data provides an experimental benchmark for the optimal choice of functional. The illustration of the model shown in Fig. 3 for the adatom structure shows rather clearly how the presence of adatoms changes the shape of the molecule. Some of the cyano CN bonds point down to the surface to interact with undisturbed Ag surface atoms, others point out of the surface to bond to Ag adatoms. This gives rise to the *average* planarity of the molecule, which has indeed become more flexible due to the charge transfer, but the consequence of this flexibility is twisting rather than bending.

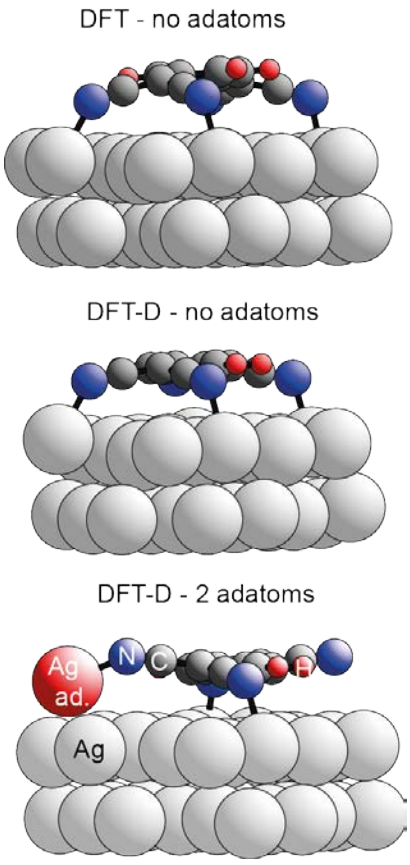

Fig. 3. Side views of a single TCNQ molecule adsorbed on Ag(111) in different structural models, as obtained from the DFT calculations with (DFT-D) and without (DFT) dispersion corrections.

With hindsight the presence of the Ag adatoms in this structure is not too surprising. The electron transfer from the metal to the adsorbed TCNQ molecules leads to them having strongly repulsive local dipoles, so one would not expect these molecules to form quite closely spaced ordered structures. The presence of Ag adatoms offers the possibility that these can act as counter-ions to stabilise the structure. Indeed, coadsorption of TCNQ with (other) metal atoms is known to lead to well-ordered two-dimensional metal-organic-frameworks (MOFs) (e.g. F_4TCNQ+Mn on Au(111) [26] and on Ag(100) [27]). In the absence of such co-deposited metal atoms, atoms extracted from the metallic substrate can play a similar role.

Of course, a key role that STM images with atomic resolution can play in structural studies is to provide strong clues to possible structural models. These are the models that may be refined in DFT calculations. Because the technique effectively samples the variations in electron densities just *above* the surface atoms, STM images provide no direct information on subsurface atoms, but might be expected to detect the presence of adatoms on a surface. In at least one closely-related example, namely F_4TCNQ on Au(111) [26], this does appear to be the case. Bright protrusions between the molecules in STM images for this system were assumed to be associated with Au adatoms and DFT calculations were used to optimise the implied structural model. A very recent investigation of this system using surface X-ray diffraction has provided direct evidence of the presence of these Au adatoms [28].

By contrast, STM images of the Ag(111)/TCNQ surface phase described above do *not* show any protrusions that could be ascribed to the presence of the Ag adatoms. Moreover, the simulated STM image of this surface, based on the DFT-D calculations of the optimised structural model (using the WSxM software package [29]), in this case including three Ag adatoms per unit mesh, fail to show any adatom-related features at the known positions of these atoms in the model (Fig. 4). In particular, the superimposed red open circles in Fig. 4 mark the locations of the Ag adatoms in the structural model used for these calculations; these do not correspond to protrusions in the simulated image.

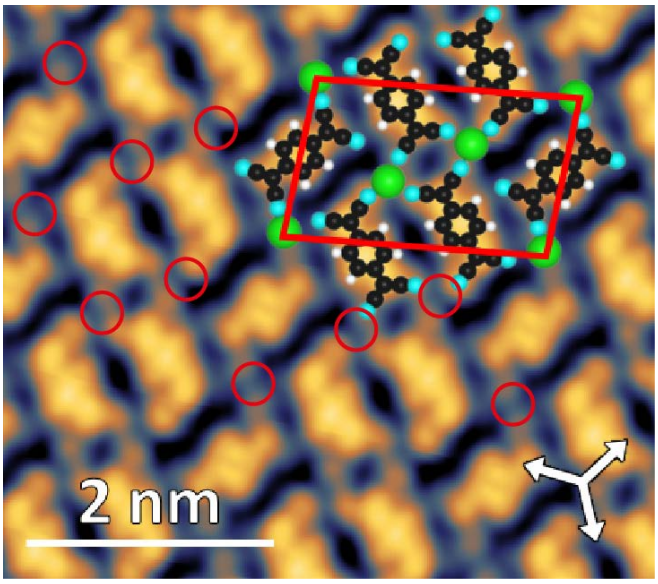

Fig. 4. Simulated STM image of the Ag(111)-TCNQ commensurate phase with the real-space structure used in calculations superimposed on the upper right-hand part of the image. Open red circles mark the adatoms positions over other parts of the image not obscured by the overlaid structural model. Adapted from ref. [24].

A qualitatively similar effect was reported in STM studies of deprotonated benzene-carboxylic acids (specifically, terephthalic acid- TPA) on Cu(110) [30] in which two different Cu adatom-molecule complex phases are believed to occur. One of these phases was proposed to involve one-dimensional Cu-adatom-carboxylate chains with pairs of Cu atoms between the molecules, while the other was proposed to comprise species with a single Cu atom between each carboxylate species. These are shown schematically in Fig. 5. These surface phases were investigated only by STM and DFT, so these structural models have not been tested against quantitative structural experiments, but comparison of the simulated STM images with the structural models used for these simulations show that the single linking Cu atoms is predicted to give rise to no visible protrusion in the image, while the pairs of Cu atoms are predicted to appear as a single protrusion. The implication in this case, too, is that metal adatoms in these molecule-metal systems are not always expected to be directly 'visible' in STM.

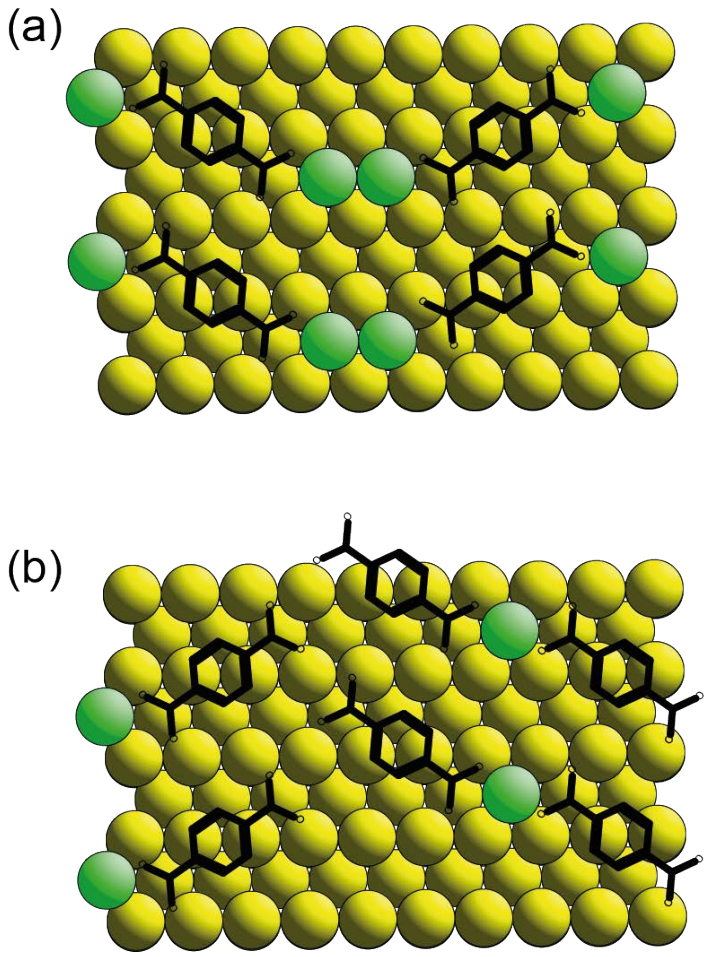

Fig. 5 Schematic diagram showing the structures proposed by Wang *et al.* [30] for two phases of terephthalic acid (TPA) on Cu(110). In (a) the structure involves -Cu-TPA-Cu-Cu-TPA-Cu- chains, while in (b) TPA-Cu-TPA units are ordered on the surface. The green spheres represent Cu adatoms, the yellow spheres represent unreconstructed substrate Cu atoms.

Of course, these simulated images are based on the simplified Tersoff-Hamman theory [31] which takes no explicit account of the properties of the probing tip; this is the standard method that is widely used to allow comparison of experimental STM data with the structural conclusions of DFT calculations and is incorporated into many standard DFT software packages. More realistic methods have been developed (e.g. [32]), but are rather rarely used in interpreting experimental STM images. The intrinsic insensitivity of STM to structural changes below the outermost atoms clearly provides a limit on the extent to which *any* combination of experimental imaging and image simulations can 'determine' a surface structure. What is less clear is how reliable comparisons of experimental images and those simulated by the standard Tersoff-Hamman approach can be used a reliable way of distinguishing certain alternative structural models. For example, an investigation of TCNE (tetracyanoethelene) on Cu(100) by STM and DFT

[33] considered two alternative structural models, one involving Cu adatoms, the other without adatoms (in the latter model the DFT calculations predicted a significant rumpling of the underlying outermost Cu(100) surface layer). The authors concluded that the no-adatom model was to be preferred on the basis of a better match of the predicted STM image to that measured experimentally, despite the fact that the DFT calculation appeared to find the adatom model to be significantly energetically favoured. This would certainly seem to be a system that would benefit from a quantitative experimental structural study.

5. Conclusions

STM and DFT have both proved to be exceptionally valuable in advancing surface science, but they are not, in isolation, an adequate replacement for the multi-technique approach to understanding surfaces developed from the 1970s. The problem is particularly significant in quantitative structural investigations, because STM can provide only very limited qualitative information, with *all* structural parameter values being provided only by the DFT calculations. Theory is never an adequate replacement for experiment where good experimental methods are available, as in surface structural investigations. As a complement to experiment, however, it can be invaluable, helping to understand *why* particular structures form.

References

1 D.P. Woodruff, *Modern Techniques of Surface Science, 3rd Edition*, Cambridge University Press, 2016.

2 D.P. Woodruff, Curr. Opin. Sol. State Mat. Sci. **7**, 75 (2003).

3 E. Kopatzki, and R.J. Behm, Surf. Sci. **245**, 255 (1991).

4 C. Klink, L. Olesen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, and N.D. Lang, Phys. Rev. Lett. **71**, 4350 (1993).

5 P. Sautet, Chem. Rev.**97**, 1097 (1997).

6 P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).

7 C. Guo, Z. Wang, D. Wang, H.-F. Wang, and P. Hu, J. Phys. Chem. C **122**, 21478 (2018).

8 M.J. Harrison, D.P. Woodruff, and J. Robinson, Surf. Sci. **600**, 340 (2006).

9 D.J. Coulman, J. Winterlin, R.J. Behm, and G. Ertl, Phys. Rev. Lett. **64**, 1761 (1990).

10 F. Jensen, F. Besenbacher, E. Lægsgaard, and I. Stensgaard, Phys. Rev. B **41**, 10233 (1990).

11 Y. Kuk, F.M. Chua, and P.J. Silverman, J.A, Meyer, Phys. Rev. B **41**, 12393 (1990).

12 F.M. Chua, Y. Kuk, and P.J. Silverman, Phys. Rev. Lett. **63**, 386 (1989).

13 H. Grönbeck, A Curioni, and W. Andreoni, J. Am. Chem. Soc **122**, 3839 (2000).

14 D.P. Woodruff, Phys. Chem. Chem. Phys. **10**, 7211 (2008).

15 L.M. Molina, and B. Hammer, Chem. Phys. Lett. **360**, 264 (2002).

16 Y. Morikawa, C.C. Liew, and H. Nozoye, Surf. Sci. **514**, 389 (2002).

17 H. Kondoh, M. Iwasaki, T. Shimada, K. Amemiya, T. Yokohama, T. Ohta, M. Shimomura, and K. Kondo, Phys. Rev. Lett. **90**, 066102 (2003).

18 M.G. Roper, M.P. Skegg, C.J. Fisher, J.J. Lee, D.P. Woodruff, and R.G. Jones, Chem. Phys. Lett. **389**, 87 (2004).

19 M. Yu, N. Bovet, C. J. Satterley, S. Bengió, K. R. J. Lovelock, P. K. Milligan, R. G. Jones, D. P. Woodruff, and V. Dhanak**,** Phys. Rev. Lett**. 97**, 166102 (2006).

20 P. Maksymovych, D. S. Sorescu, and J. T. Yates, Jr. Phys. Rev. Lett., **97**, 146103 (2006).

21 J.P. Prated Ramalho, J.R.B. Gomes and F. Illas, RSC Advances, **3**, 13085 (2013).

22 R.J. Maurer, V.G. Ruiz, J. Canarillo-Cisneros, W. Liu, N. Ferri, K. Reuter and A.T. Tkatchenko, Prog. Surf. Sci. **91**, 72 (2016).

23 J.P. Janet, Q. Zhao, E.I. Ioannidis and H.J. Kulik, Molecular Simulation **43**, 327 (2017).

24 P.J. Blowey, S. Velari, L.A. Rochford, D.A. Duncan, D.A. Warr, T.-L. Lee, A. De Vita, G. Costantini, and D.P. Woodruff, Nanoscale **10**, 14984 (2018).

25 D.P. Woodruff, B.C.C. Cowie, and A.R.H.F. Ettema, J. Phys. Condens. Matter **6**, 10633 (1994).

26 M.N. Faraggi, N. Jiang, N. Gonzalez-Lakunza, A. Langner, S. Stepanow, K. Kern, and A. Amau, J. Phys. Chem. C **116**, 24558 (2012).

27 T.-C. Tseng, N. Abdurakhmanova, S. Stepanow, and K. Kern. J. Phys. Chem. C **115**, 10211 (2011).

28 P.J. Mousley, L.A. Rochford, H. Hussain, C. Nicklin, G. Bell, and D.P. Woodruff. To be published.

29 I. Horcas, R. Fernández, J.M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baró. Rev. Sci. Instrum., **78**, 013705 (2007).

30 Y. Wang, S. Fabris, T.W. White, F. Pagliuca, P. Moras, M. Papagno,D. Topwal, P. Scheverdyaeva, C. Carbone, M. Lingenfelder, T. Classen, K. Kern,and G. Costantini, Chem. Commun. **48**, 534 (2012).

31 J. Tersoff, and D. R. Hamann, Phys. Rev. B, **31,** 805 (1985).

32 W.A. Hofer, A.S. Foster, and A.L. Schuger, Rev. Mod. Phys. **75**, 1287 (2003).

33 S. Bedwani, D. Wegner, M.F. Crommie and A. Rochfort, Phys. Rev. Lett. **101**, 216105 (2008)